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FI-STM INVESTIGATION OF ATOMIC HYDROGEN ADSORPTION ON THE Si(100)2x1 SURFACE

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FI-STM Investigation of Atomic Hydrogen Adsorption on the Si(100)2x1 Surface

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Abstract

A field ion-scanning tunneling microscopy study on hydrogen chemisorption on the Si(100)2x1 surface is presented. At low coverages, hydrogen atoms reside singly on top of the dimerised Si atoms, and are imaged brightly. The hydrogen chemisorption induces the buckling of dimers, indicating the strong bonding between Si and H atoms. With increasing coverage, both the 2x1 monohydride and 1x1 dihydride phases were formed. The former is imaged dark compared with the unreacted Si dimers, due to the reduction of the density of electronic states near the Fermi level. Surface etching was also observed. It was found that the corrosion of the surface is modest in the monohydride phase, while during the formation of the dihydride phase, the corrosion becomes significant. The behaviour of hydrogen desorption from the dihydride and monohydride phases was investigated as a function of annealing temperature. Our STM results support the mechanism that the desorbing H_2 molecules are formed by combination of two hydrogen atoms forming the dihydride phase. Upon annealing at elevated temperatures, the Si overlayer stripes are formed by desorption of hydrogen from the etching products and the rearrangement of the Si atoms.

1. Introduction

The chemisorption of atomic hydrogen on various silicon surfaces has been studied for several decades[1]-[4] because of its importance in both fundamental research and technological applications. For instance, it is well known that hydrogen passivates silicon surfaces by saturating the silicon dangling bonds, other electronically active defects and stabilizing grain boundares, etc. In addition to that, the adsorption of hydrogen on Si surfaces also provides a model example for investigation of the surface reconstructions and bonding properties. Though the atomic hydrogen adsorption on the Si(100) 2x1 surface has been extensively studied by various kinds of methods, many controversies still exist. Previous studies have confirmed the existence of three reconstructions induced by hydrogen adsorption at different conditions, i.e. 2x1[2],[5] (the monohydride phase), 1x1[2](the dihydride phase), and the 3x1[3] phase. By modest adsorption of atomic hydrogen at room temperature or saturate adsorption at elevated temperature (about 250^0C), the 2x1 phase can be formed, which characterised by binding one hydrogen atom to the dangling bond on each dimerised silicon atom without breaking the dimer bond. By saturating surface with hydrogen at room temperature, Sakurai and Hagstrum[2] discovered the 1x1 reconstruction and introduced the idea of the dihydride phase, which formed by adsorbing two hydrogen atoms on each Si atom accompanied by the interruption of the dimer bond. Yet, the geometry of the hydrogen atoms in this phase has not been identified unambiguously. Recently, Chabal and Raghavachari[3] found a new 3x1 phase at saturation coverage while holding the substrate temperature at about 100^0C. This reconstruction is formed by alternating arrangement of the monohydride and dihydride rows and appears even more stable than either the monohydride phase or the dihydride phase over a certain range of chemical potential[6]. The electronic structures of the 2x1 monohydride phase and 1x1 dihydride phase have been investigated by Sakurai and Hagstrum[2] and Ciraci, *et al*[7] using UPS, and by Maruno, *et al*[8],[9] using EELS, etc. It was found that the hydrogen induced electronic states are located at about -12eV and -10eV with respect to the vacuum level for the monohydride phase and dihydride phase, respectively[2]. From TPD

(Temperature programmed desorption)[10] experiment, Gupta *et al* derived that desorption of H_2 from both the monohydride and dihydride phases exhibits second-order kinetics. However a previous investigation[11] and more recent LITD(laser induced thermal desorption) experiment[12] suggested a first-order desorption kinetics for desorption of H_2 from the both phases.

The corrosion of the surface upon hydrogen adsorption has also been noticed and investigated mainly by desorption experiments. The products of the reaction have been identified to be mainly SiH_3 and small fractions of Si_2H_6, Si_3H_8 and Si_4H_{10}, etc[13], but the detailed process and etching mechanism are still unclear. Moreover, earlier conclusions were based on the data averaged over the macroscopic area. The observation of the surface structure in real space had not been possible untill the invention of the scanning tunneling microscope by Binnig and Rohrer[14]. The STM has proven to be of great potential to study the surface geometry as well as the surface electronic states with atomic resolution in real space. Hamers, *et al*[15] imaged the monohydride phase produced by dissociative adsorption of NH_3 on the Si(100)2x1 surface. The imaged feature was attributed to the tunneling current through the localized Si-H bonding orbitals with a sample bias of -2V. However, Johansson, *et al*[16] concluded, based on their polarization-dependent ARPES experiment, that the highest energy position of this band was 4.7eV below the Fermi level and that no H-induced structures should be visible at all in the energy ranging from 0 to -2eV, in contrary to the Hamers *et al*'s STM study. Recently Boland reported the observation of the newly discovered 3x1 phase[17] and discussed the role of pairing in the recombinative desorption of hydrogen[18]. However, the understanding of this system is far from completeness and many controversies remain unsolved.

In this paper, we will present our FI-STM investigations on the hydrogen chemisorption on the Si(100)2x1 clean surface. In the following sections, after brief description of our experimental arrangement, we will present the behaviour of adsorbed hydrogen atoms at the initial stage of adsorption, then we will show the surface structure of the monohydride phase and dihydride phase, and the corrosion of the surface caused by

hydrogen adsorption. At last we will show the surface change upon desorption at different temperatures. The mechanism behind the presented results will also be discussed.

2. Experiment

The details of our FI-STM system have been described elsewhere[19]. Here is a brief description. Our FI-STM is a combination of a high performance scanning tunneling microscope(STM) and a room temperature field ion microscope(FIM) which is used for the precise characterization of the scanning tip and its atomic scale fabrication. The entire STM setup is suspended with three 100cm-long springs and a 12-piece set of magnetic eddy current damper which is attached beneath the STM set. The entire FI-STM chamber is mounted on the so-called active damper. By doing so, the troublesome resonance frequencies at 1 to 3 Hz are completely eliminated, making it possible to operate the STM stably and reliably. The use of the <111> oriented single crystal tungsten tip provides us with needed stability and long-lifetime of several months with daily operation. The main UHV chamber is pumped by a 1200l/s custom-design Riber ion pump and the base pressure is below $3x10^{-11}$ except for the time of annealing the sample up to 1220^0C. The pressure rise during the final annealing do not go beyond $1x10^{-10}$ torr with this fast pumping system.

The Si(100) sample used was cut into a 4x19 mm^2 piece from a Sb doped n-type commercial Si(100) wafer with r about 0.07 W· cm. Prior to introducing the sample into the UHV FI-STM chamber, only washing with methyl-alcohol was administered for sample cleaning. Cleaning the sample in the UHV preparation chamber (which is attached to the main chamber) was carried out by a series of heating up to 1220^0C following the 5-hour's degassing at 700^0C. In this way, the clean Si(100)2x1 surface with a minimum density of defects was obtained. The temperature was measured by an infrared pyrometer.

The atomic hydrogen dosing was achieved by introducing high purity H_2 gas into the UHV chamber through an adjustable leak valve, passing through the hot tungsten ribbon which was heated up to 1760K to dissociate molecular hydrogen into atomic hydrogen. The H_2 dosage, which was given in Langmuirs, was used only as a measure for the atomic hydrogen deposition rate. It was ensured that the hot tungsten ribbon did not damage the

vacuum during H exposure. The hydrogen adsorption was performed by holding the sample at room temperature. Some temperature rise in the sample surface was expected during the H adsorption, however, the tempetature rise was not high enough to cause the desorption of the atomic hydrogen from the surface. The STM images were taken at least 3 hours after the annealing to avoid the effect of thermal drift. Sample bias between -3 to +3V was used and the tunneling current was kept constant at 20pA during the normal STM operation.

3. Results and discussion

3.1. Properties of the initial stage of hydrogen adsorption

Fig.1 is a typical STM topograph of atomic hydrogen adsorbed on the Si(100)2x1 surface at a very low coverage(~0.03ML). The surface is characterised by the bright round spots sitting on top of the buckled dimers and distributed randomly on the surface. At the both sides of these bright spots, the dimers are also buckled, imaged brighter than the unbuckled dimer chains. Based on the fact that the number density of these bright spots increases with the hydrogen dosage, these are concluded to be the image of hydrogen atoms. This is basically consistent with the result reported by Boland[18], though he couldn't observe the buckling of the dimers adjacent to the hydrogen atoms. A question is whether it is hydrogen atoms that prefer to stay on buckled dimers or the buckling of the dimers is induced by the adsorbed hydrogen atoms. From the following argument, we conclude that it is hydrogen atoms that induce the buckling of the dimers adjacent to them, though it is still possible that H atoms prefer to stay on buckled dimers. First, by comparing the density of the buckled dimers before and after adsorption, it was found that the density of this kind of buckled dimers increased with the increasing H dosage. Secondly, the adatom-like protrusions without buckling of the adjacent dimers were rarely found. The buckling of the dimers on the Si(100)2x1 surface has been interested for many years and there are controversies between the results obtained from STM and other techniques. Results from the STM[20] have suggested that the surface seems mostly unbuckled. However, it has been revealed that the energy difference between the buckled dimer and

unbuckled dimer is small enough so that the STM imaged symmetric dimers may in fact be the time average of the rapidly oscillating asymmetric(buckled) dimers with charges transferring back and forth between two dimerised atoms[21], [22], while dimers can be stably buckled in the vicinity of steps and various kinds of point defects[20]. The fact that the H atoms are almost bonded singly with Si atoms instead of in pairs at low coverages indicates that bonding between the H atom and the dangling bond on top of one of the dimerised Si atom is so strong that most of the arrived H adatoms adsorbed on the dangling bonds without moving around. So because of this strong bonding, as well as the saturation of the dangling bond by adsorbed hydrogen atom, the periodicity and the symmetry around the adsorption site no longer exist, thus the charge redistribution is unavoidable, which is likely to induce the buckling of the dimers nearby. Similar results were also obtained on alkali-metal adsorption on the Si(100)2x1 surface[23] by STM. From the number of buckling dimers induced by H adsorption, we suggest that the interaction between H atom and Si substrate is of short range, i.e., limited to one or two dimers near the adsorbed H atom. It is interesting and important to study the interaction between the singly adsorbed hydrogen atoms with surface silicon atoms as well as the interactions among the adsorbed hydrogen atoms through the investigation of the initial stage of hydrogen adsorption, which may reveal the mechanism of the desorption process[18]. However, up ot now, little work has been done on it, which limits our further discussion. We hope our resuits will stimulate further investigations of the detailed properties of the Si-H bond, such as the charge transfer, bonding length, and electronic states, etc.

3.2. Formation of the monohydride phase and dihydride phase

Figures 2(a)-(d) are the STM images showing the changes of the surface structure with increasing H_2 coverage. Fig. 2(a) is the image obtained after 24L's adsorption, the coverage is estimated to be approximately 0.3ML. In this case, the surface is characterized by the interruption of the dimer chain by dark areas and the buckling of almost all the dimers on the surface which imaged bright. With increasing coverage, the area of dark contrast increases, as shown in Fig. 2(b), which was obtained upon 48L's exposure. In this case,

the dimer chains in the dark area are well resolved, showing clearly that the dimers in the monohydride phase are imaged dark. This can be explained by the reduction of the electronic density of states near the Fermi level[25][26]. From the UPS results[7]-[24] and theoretical calculation[27], it is known that on the clean dimerised Si(100)2x1 surface, there exists a localized surface state near the Fermi level due to the dangling bond of the surface silicon atoms. This surface state is removed upon hydrogen adsorption by saturation of the dangling bonds, resulting in the reduction of the tunneling current.

When the surface is largely covered by the monohydride phase, the prominent feature is the bright dots on the well ordered 2x1 monohydride surface(see also Fig. 2(b)). These bright dots can be grouped into two types, namely type A and B. Fig. 3 is a close-up illustrating typical images of dots "A" and "B", where "A" dots are located on the side of the dimer chains, while "B" dots are located on the dimer chains and imaged larger than "A" dots. According to the observation that (a) the dimers adjacent to "A" dots are rarely buckled, which is in contrast to the results in the initial stage of hydrogen adsorption, and that (b) the density of "A" dots decreased with the increase of the hydrogen coverage, we suggest that "A" dots represent the unpaired hydrogen atoms. Thus the unbuckling of the dimers adjacent to the "A" dots indicate the considerable passivation of the surface reactivity. On the other hand, the density of type "B" dots remains almost unchanged. Further increasing the dosage results in the formation of small amounts of clusters imaged slightly larger than "B" dots. Though the identification of the products by STM alone is not possible, we suggest that these type "B" dots are the products of reacted Si atoms with hydrogen, according to the thermal desorption results by Gates *et al*[13], mainly SiH_3 with small amount of other species, such as Si_2H_6, Si_3H_8 and Si_4H_{10}. Fig. 2(c), was obtained upon 108L of hydrogen exposure, where type "A" dots were almost eliminated, while type "B" dots remained. It is also found from our STM investigation that these products spread randomly and almost separately on the surface, with little tendency to combine into larger clusters, indicating the absence of etching centers or nucleation centers of the reacted Si atoms. During the formation of the monohydride phase, the degree of surface etching is still limited within a low level, which let the monohydride phase form with higher order. Also in

the case as shown in Fig. 2(c), it was found that the formation of a new phase, the dihydride phase, started, indicated by the splitting of the monohydride dimers.

With increasing dosage, the surface gradually shifts from the 2x1 monohydride phase to the dihydride phase. Fig. 2(d) shows the surface upon 2000L of hydrogen adsorption. The surface is of the 1x1 reconstruction with a fraction of the 2x1 phase. We noticed that with the increase of the proportion of the 1x1 phase, the etching of the surface becomes more and more extensive, shown by the high density of missing atom defects and "B" dots. The difference between the sizes of the dots is slight, indicating that the bonding to the substrate is still strong enough to resist the migration of the reacted species.

3.3. Desorption of hydrogen

The understanding of the desorption properties of hydrogen is almost of the same importance as the adsorption process, especially in controlling of the epitaxial growth of the Si film on the Si(100) surface by CVD, as well as analyzing the surface etching process. For many years, several groups have studied the properties of the desorption process[10],[12],[13]. The desorption temperatures for hydrogen in the SiH species (b_1 state) and SiH_2 species (b_2 state) have been determined by several reports with similar conclusions. Gupta, *et al*[10] reported that for hydrogen adsorbed on porous silicon, which is similar to that on the Si(100) surface according to the similarities between the infrared spectra of hydrogen in both cases, the desorption of hydrogen in the b_1 state occurs at temperatures between 720-800K(447-527^{0}C), while the desorption of hydrogen in the b_2 state occurs at 640-700K(367-427^{0}C). From TPD spectra, Gates, *et al* [13] found that the peak temperature for H_2 desorption from the b_1 state is 540^{0}C and the desorption starts at about 450^{0}C, while the peak temperature for desorption of the b_2 state is 425^{0}C and the desorption starts at about 370^{0}C. So these results suggest the desorption of hydrogen start about 370^{0}C for the b_2 state and 450^{0}C for the b_1 state. Gates, *et al*[13] also found that the desorption of the SiH_3 species occurs at about 375^{0}C in the form of SiH_4, which is 50^{0}C below the desorption peak of b_2 state. The desorption of SiH_4 also results in the removal of the silicon atoms from the top of the surface. The TPD yield of SiH_4 saturates at the

maximum value when the coverage increased beyond 0.5ML. Recently, Boland[18] reported STM data on the behaviour of the monohydride phase upon H desorption. However, controversies about the desorption kinetics and transition process from the dihydride phase to the monohydride phase remain. And information on the real space observation of the surface structure change upon H_2 desorption is still not sufficient, especially in the process of the desorption from the dihydride phase.

To investigate the desorption process of hydrogen from both the SiH_2 state(b_2) and SiH state(b_1), the surface was exposed to 1000L of hydrogen prior to annealing at modest temperatures. As shown in fig. 4(a), the surface is of mixture of the 1x1 and 2x1 phases. According to the temperature dependence of the H_2 desorption in each species, we performed sequential annealings, i. e. heating the sample for 1 min at temperatures: 320^0C, 400^0C, 460^0C and 500^0C.

Annealing the sample at 320^0C resulted in no obvious changes in the surface structure, which is consistent with the TPD result at the same temperature, that is, almost all the adsorbed hydrogen atoms and reacted species remain on the surface. Though some of the hydrogen atoms may obtain sufficient energy to desorb from the surface due to the Boltzmann distribution of thermal energy, the amount is small in such a short time duration as was shown by an isothermal desorption experiment[10]. After further annealing of the sample at 400^0C for 1 min, as shown in fig. 4(b), the surface is characterised by a high density of dark defects and some bright dots which made the surface look highly disordered. However the direction of the dimer chain can still been identified, indicating that it is of the 2x1 reconstruction. We attribute this change to desorption of the hydrogen in the b_2 state, while the monohydride phase still exists. There exists controversy about the way of H_2 desorption from the dihydride state. Schulze *et al*[11] and Masson *et al*[28] had suggested that the desorbing H_2 was formed by the association of the two hydrogen atoms in the same SiH_2 species in order to explain the suggested first-order desorption kinetics. In contrast, theoretical work[29] assumed the desorption of H_2 from the dihydride species on Si(100) in terms of the recombinationary desorption of two hydrogen atoms from two adjacent silicon hydride species. In this case, the transition into the monohydride phase

takes place spontaneously with the combination of hydrogen molecules. This model supported the second-order desorption kinetics obtained from the isothermal desorption experiment[10]. However, as can be seen in fig. 4(b), the surface is highly disordered due to the interruption of the dimer chain by dark areas which are attributed to the monohydride phase from our previous analysis. This suggests that H_2 molecules desorb directly from the dihydride phase without shifting to the monohydride phase. Because of the complicated processes involved in the adsorption and desorption of hydrogen, though it might be difficult to rule out unambigously one of the desorption models suggested above, we suggest, from the STM observation, that at least a large amount of hydrogen in the dihydride phase desorb directly from the surface without transiting into the monohydride phase. Thus our STM result supports the assumption that the desorbing H_2 molecules are formed by the two hydrogen atoms in the same SiH_2 species instead of two adjacent SiH_2 species. This is in contradiction with TPD data[10],[30], however, TPD data did not give an unambiguous answer to the kinetics of H_2 desorption in dihydride phase as no TPD work gave the absolute coverage change before and after desorption of the dihydride phase. In fact, the desorption kinetics of H_2 from the Si(100) surface has not been well understood yet, the previous analysis of TPD data was merely based on the assumption that dihydride phase transferred to monohydride phase by desorbing H_2 from two dihydride species. As to our knowledge, only Oura *et al*'s work[31] shows the absolute coverage change of the adsorbate from 1.85ML of hydrogen saturated 1x1 phase to 1ML of the 2x1 monohydride phase. However, this result dose not have enough accuracy to convince people since an ideally saturated 1x1 phase should be 2ML instead of 1.85ML. Further more, no other work has ever been published to support this conclusion. Upon further annealing of the sample at 460^0C for 1 min, the surface is as shown in fig. 4(c), which is dominated by the 2x1 structure with ordered dimer chains, although the density of defects is still higher than that on the clean surface. A novel feature in fig. 4(c) is the formation of the adatom lines on the substrate terraces, while the number of bright dots decreases considerably, indicating the reformation of the clean Si(100)2x1 surface. By correlating the disappearance of the bright dots and the formation of the adatom lines, we attribute these adatom lines to Si atoms that

formed by desorption of hydrogen from SiH_3 and small amounts of other species. The mobility of dissociated Si atoms is high enough so that the Si atoms can combine with each other with high probability, forming epitaxial dimer lines perpendicular to the direction of the dimer lines of the substrate. Further annealing of the sample at 500^0C results in no obvious changes in the surface structure, indicating that the critical temperature for Si overlayer formation is between 400^0C and 460^0C.

4. Summary

Our STM investigations of H adsorption on the Si(100)2x1 surface can be summarized as follows(see Fig.5 for illustration).

1. At low coverages (below 10% of one monolayer), single hydrogen atoms reside on the top of the dimerised surface Si atoms, imaged as bright spots. Those H atoms also induce the buckling of the dimers at the both sides of the adsorbed hydrogen atom.
2. With increasing coverage, the density of hydrogen atoms which adsorb in pairs increases. The monohydride phase is imaged dark compared with unreacted Si dimers because of the reduction of the density of states near the Fermi level.
3. Our data suggest that the reacted Si atoms, mainly SiH_3, are imaged as bright dots, spreading randomly on the dimer chain. At the monohydride phase, the surface etching is slight, while upon the formation of the dihydride phase, the corrosion of the surface becomes significant. It seems that the etching originates and expands randomly without any preferred sites.
4. Upon annealing a surface having a mixture of the 1x1 and 2x1 phases at different temperatures, the changes in the surface structure were observed. Upon annealing at 400^0C, the dihydride phase disappeared while the monohydride phase still existed. Our result support the assumption that the desorbing H2 molecules are formed by combination of two hydrogen atoms in the same SiH_2 species. Upon annealing the sample at above 460^0C, the 2x1 monohydride phase disappeared, the surface is dominated by the 2x1 Si dimers with overlayer stripes formed by the recombination of Si atoms through the dissociation of SiH_3 species.

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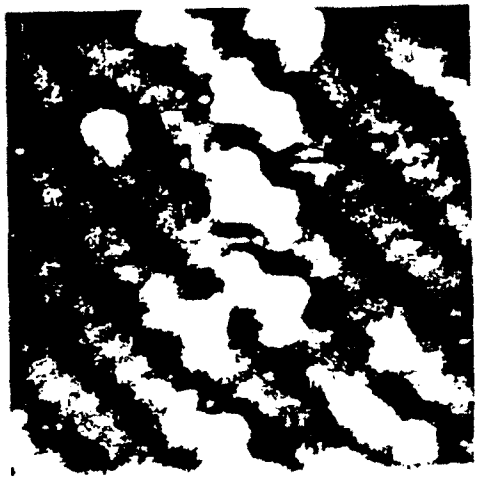


Fig. 1.

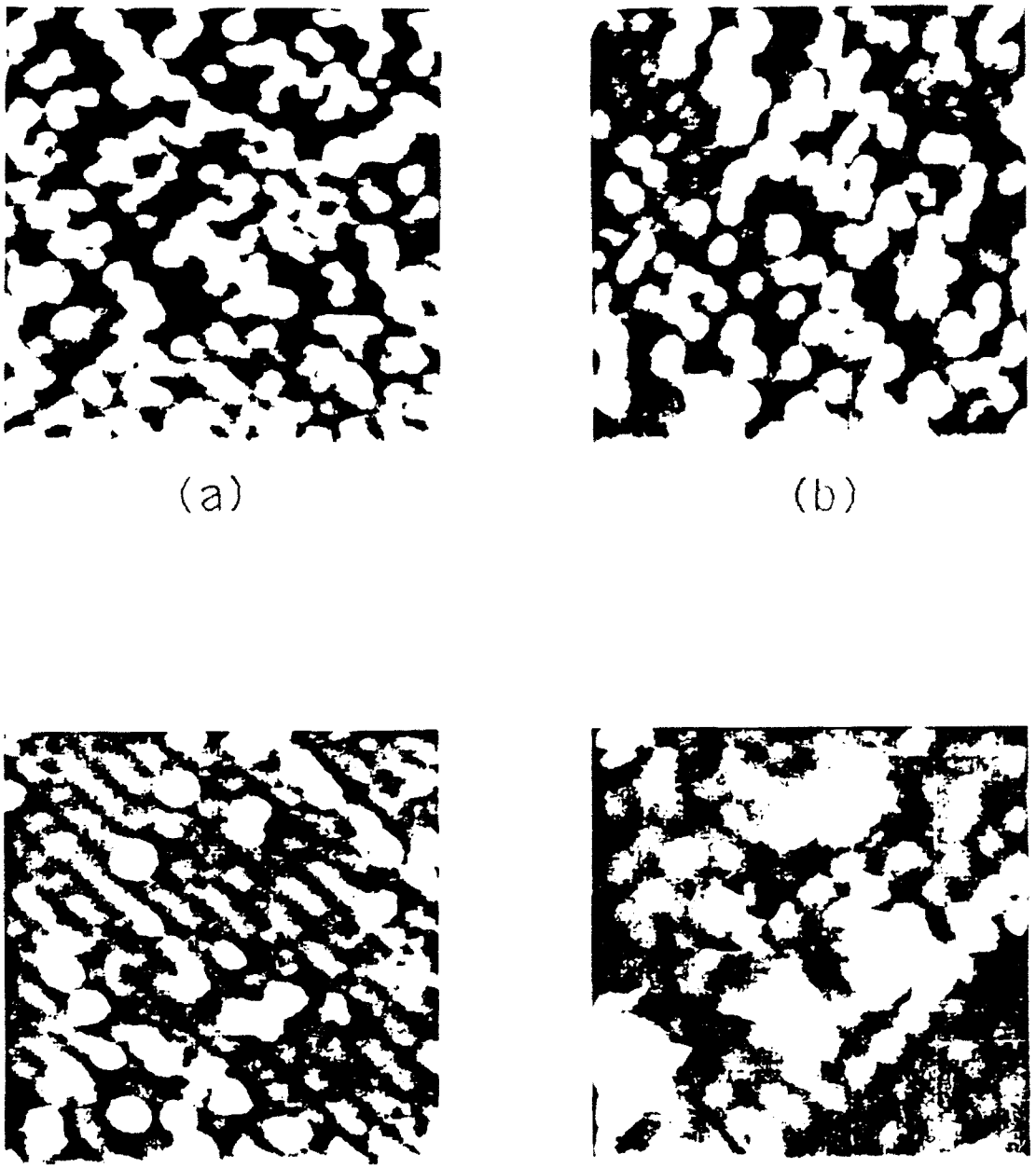
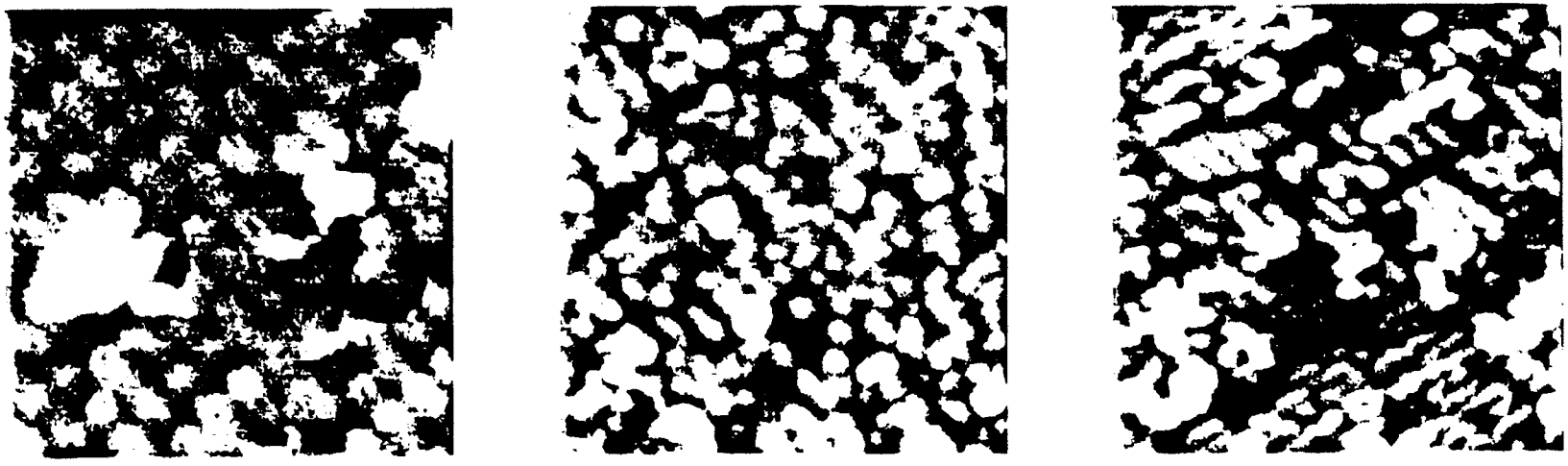


Fig. 2.

Fig. 3.



(a) (b) (c)

Fig. 4.

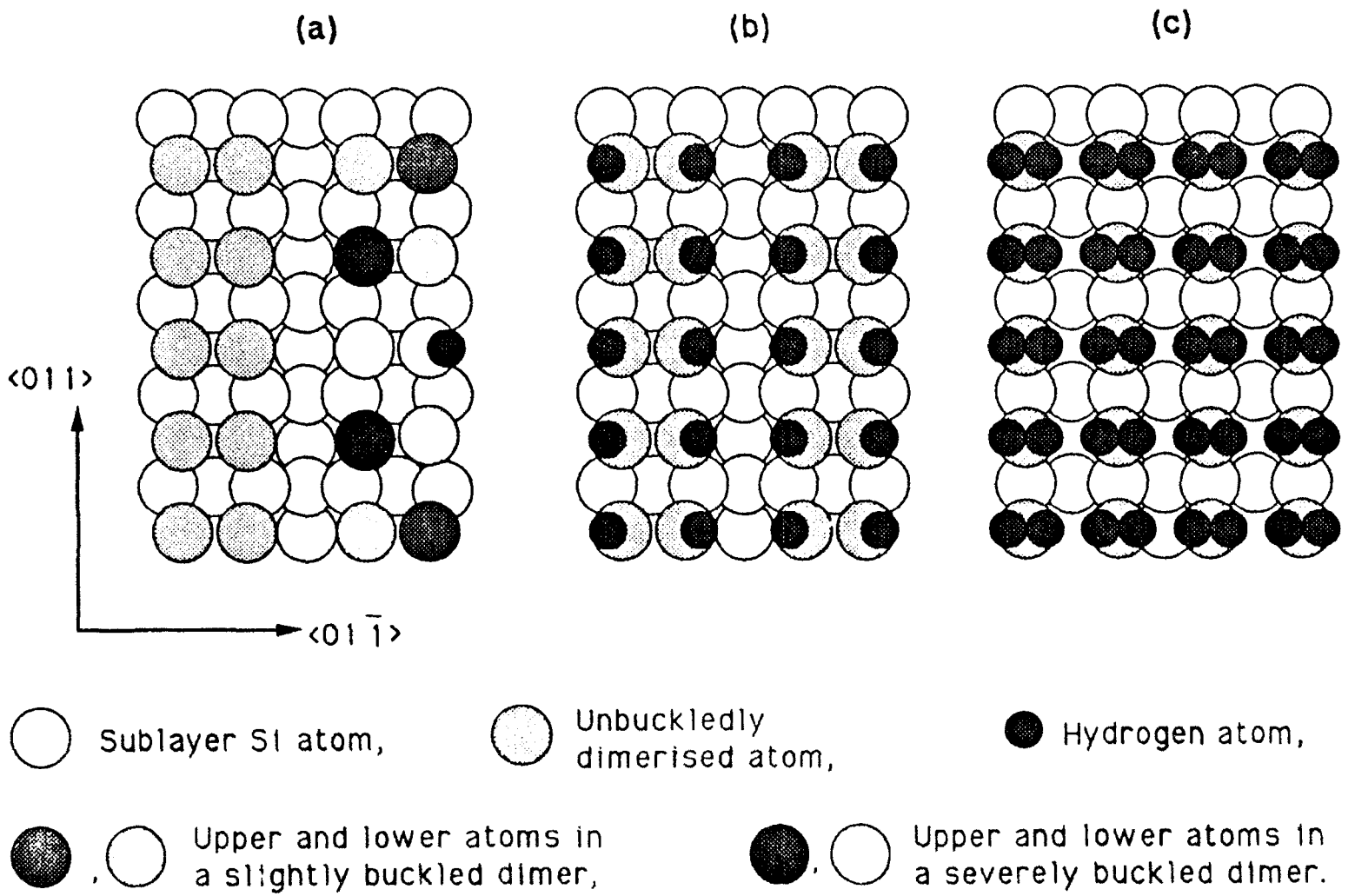

(a)
(b)
(c)
<011>
<01 $\bar{1}$>
Sublayer Si atom,
Unbuckledly dimerised atom,
Hydrogen atom,
Upper and lower atoms in a slightly buckled dimer,
Upper and lower atoms in a severely buckled dimer.

Fig. 5.

Figure Captions

Fig. 1. STM topography of Si(100)2x1 surface covered by about 0.03ML of atomic H, sample bias V_S=1.6V.

Fig. 2. Si(100) surface structures after hydrogen adsorption at different dosages. (a) After 24L of adsorption, V_S=-2.0V, (b) After 48L of adsorption, V_S=-3.0V, (c) After 108L of adsorption, V_S=-1.6, and (d) After 2000L of adsorption, V_S=-2.0V. The area is about 100x100 $Å^2$ for (a)-(c), and about 43x43$Å^2$ for (d), respectively.

Fig. 3. The illustration of two different kinds of features, marked by "A" and "B" respectively. The image was obtained upon 48L's exposure, V_S=-2.0V.

Fig. 4. Changes in surface structure upon annealing at different tempetature. (a)Mixture of monohydrogen and dihydrogen after 1000L of hydrogen adsorption without annealing. (b)After annealing at 400^0C, and (c)After annealing at 460^0C. V_S=-1.6V for all three. The area is about 150x150$Å^2$ for (a) and (b), and about 43x43$Å^2$ for (c), respectively.

Fig. 5. Schematic of the adsorption geometry of hydrogen atoms, (a) initial stage of adsorption, (b) 2x1 monohydride phase, and (c) 1x1 dihydride phase.

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